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Proton-transfer compounds of isonipecotamide with the aromatic dicarboxylic acids 4-nitrophthalic, 4,5-dichlorophthalic, 5-nitroisophthalic and terephthalic acid

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The structures of the 1:1 proton-transfer compounds of isonipecotamide (piperidine-4-carboxamide) with 4-nitrophthalic acid [4-carbamoylpiperidinium 2-carboxy-4-nitrobenzoate, $C_6H_{13}N_2O_8^+ \cdot C_8H_4O_6^-$, (I)], 4,5-dichlorophthalic acid [4-carbamoylpiperidinium 2-carboxy-4,5-dichlorobenzoate, $C_6H_{13}N_2O_8^+ \cdot C_8H_3Cl_2O_4^-$, (II)] and 5-nitroisophthalic acid [4-carbamoylpiperidinium 3-carboxy-5-nitrobenzoate, $C_6H_{13}N_2O_8^+ \cdot C_8H_4O_6^-$, (III)], as well as the 2:1 compound with terephthalic acid [bis(4-carbamoylpiperidinium) benzene-1,2-dicarboxylate dihydrate, $2C_6H_{13}N_2O_8^+ \cdot C_8H_4O_4^{2-} \cdot 2H_2O$, (IV)], have been determined at 200 K. All salts form hydrogen-bonded structures, *viz.* one-dimensional in (II) and three-dimensional in (I), (III) and (IV). In (I) and (III), the centrosymmetric $R_2^2(8)$ cyclic amide–amide association is found, while in (IV) several different types of water-bridged cyclic associations are present [graph sets $R_4^2(8)$, $R_4^3(10)$, $R_4^4(12)$, $R_3^3(18)$ and $R_6^4(22)$]. The one-dimensional structure of (I) features the common ‘planar’ hydrogen 4,5-dichlorophthalate anion, together with enlarged cyclic $R_3^3(13)$ and $R_3^3(17)$ associations. In the structures of (I) and (III), the presence of head-to-tail hydrogen phthalate chain substructures is found. In (IV), head-to-tail primary cation–anion associations are extended longitudinally into chains through the water-bridged cation associations, and laterally by piperidinium–carboxylate $N-H \cdots O$ and water–carboxylate $O-H \cdots O$ hydrogen bonds. The structures reported here further demonstrate the utility of the isonipecotamide cation as a synthon for the generation of stable hydrogen-bonded structures. An additional example of cation–anion association with this cation is also shown in the asymmetric three-centre piperidinium–carboxylate $N-H \cdots O \cdots O'$ interaction in the first-reported structure of a 2:1 isonipecotamide–carboxylate salt.

Comment

Our project investigating the hydrogen-bonding modes in salts of the Lewis base piperidine-4-carboxamide (isonipecotamide; INIPA) with carboxylic acids has provided a considerable number of structures, the majority being anhydrous 1:1 salts with aromatic acids (Smith & Wermuth, 2010*d,f*, 2011*a*). Solvated examples are the nicotinate (a partial hydrate; Smith & Wermuth, 2011*c*), the acetate (a monohydrate; Smith & Wermuth, 2010*e*) and the 6-carboxypyridine-2-carboxylate (a methanol monosolvate; Smith & Wermuth, 2011*c*), while with *o*-phthalic acid a 1:1 hydrogen phthalate–phthalic acid salt adduct is formed (Smith & Wermuth, 2011*b*). Anhydrous picrates are also known (Smith & Wermuth, 2010*c*), together with a 2:1 salt with bipyridine-4,4′-disulfonate (Smith *et al.*, 2010). In the light of the unusual formation of a 1:1:1 cation–anion–phthalic acid adduct from a 1:1 stoichiometric reaction (Smith & Wermuth, 2011*b*), our further aim was to investigate the nature of the products formed from similar reactions of INIPA with a series of aromatic dicarboxylic acids in various

alcoholic and aqueous alcoholic solutions. Examples included 4-nitrophthalic acid (NPHA), 4,5-dichlorophthalic acid (DCPA), 5-nitroisophthalic acid (NIPA) and terephthalic acid (TPA), which provided good crystalline products. The 1:1 anhydrous salts of 4-carbamoylpiperidinium 2-carboxy-4-nitrobenzoate, (I), 4-carbamoylpiperidinium 2-carboxy-4,5-dichlorobenzoate, (II), and 4-carbamoylpiperidinium 3-carboxy-5-nitrobenzoate, (III), were obtained, and the 2:1 hydrated salt of the terephthalate, bis(4-carbamoylpiperidinium) benzene-1,2-dicarboxylate dihydrate, (IV), was also identified. The structures of (I)–(IV) are described here.

Figure 1

The molecular conformation and atom-numbering scheme for the INIPA cation and NPHA monoanion in (I). Displacement ellipsoids are drawn at the 40% probability level and the inter-species hydrogen bond is shown as a dashed line.

Figure 2

The molecular configuration and atom-numbering scheme for the INIPA cation and DCPA monoanion in (II). Displacement ellipsoids are drawn at the 40% probability level and the inter-species hydrogen bond is shown as a dashed line.

With the 1:1 salts, (I)–(III) (Figs. 1–4), proton transfer has occurred to the hetero N atom of the piperidine ring, while with the terephthalate salt, (IV), a two-proton transfer is involved, with the formation of a dianion. The resulting piperidinium group of the anion in each salt, together with the hydrogen donor and acceptor *p*-related substituent amide group, are subsequently involved in hydrogen-bonding interactions. These result in supramolecular structures, which are three-dimensional in (I), (III) and (IV), and one-dimensional in (II) (Figs. 5–8). A feature of the hydrogen bonding in (I) and (III) is the presence of the centrosymmetric cyclic homomolecular N–H...O hydrogen-bonded amide–amide motif (Allen *et al.*, 1998), with graph set $R_2^2(8)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995). This motif has now been found in 11 of the 24 known structures of INIPA proton-transfer salts, including the present examples.

In the structure of the 1:1 INIPA salt with 4-nitrophthalic acid, (I), the 1-carboxy rather than the 2-carboxy group is deprotonated (Fig. 1), giving a primary piperidinium–carboxylate N–H...O ion-pair interaction. The hydrogen phthalate anions form head-to-tail hydrogen-bonded chain substructures featuring short carboxy–carboxylate O–H...O hydrogen bonds [graph set $C(7)$; Fig. 5]. These substructures

Figure 3

The molecular conformation and atom-numbering scheme for the INIPA cation and NIPA monoanion in (III). Displacement ellipsoids are drawn at the 40% probability level. The inter-species hydrogen bond is shown as a dashed line.

Figure 4

The molecular conformation and atom-numbering scheme for the INIPA cation, the TPA dianion and the solvent water molecule in the asymmetric unit of (IV). The dianion has inversion symmetry [symmetry code: (i) $-x, -y + 1, -z$]. Displacement ellipsoids are drawn at the 40% probability level and inter-species hydrogen bonds are shown as dashed lines.

Figure 5

The two-dimensional hydrogen-bonded network structure of (I), extending across the bOc plane of the unit cell, showing hydrogen-bonding associations as dashed lines. Graph sets for cyclic hydrogen-bonding associations are also indicated. Non-interactive H atoms have been omitted. (For symmetry codes, see Table 1.)

Figure 6

The one-dimensional hydrogen-bonded ribbon structure of (II), extending along the *b* cell direction, showing hydrogen-bonding associations as dashed lines. Graph sets for cyclic hydrogen-bonding associations are also indicated. Non-interactive H atoms have been omitted. (For symmetry codes, see Table 2.)

are common among hydrogen phthalate salt structures (Glidewell *et al.*, 2005; Smith & Wermuth, 2010*b*). The peripherally bound INIPA anions give structure extension across (011) through classic centrosymmetric $R_2^2(8)$ amide–amide $N-H\cdots O$ hydrogen-bonded dimer associations. In addition, amide–nitro $N-H\cdots O$ and piperidinium–carboxylate $N-H\cdots O$ associations (Table 1) result in a three-dimensional structure. In the nitrophthalate anion, the carboxylate group is rotated significantly out of the benzene plane [torsion angle $C2-C1-C11-O12 = -76.7(2)^\circ$], while the carboxylic acid and nitro groups are essentially coplanar with the benzene plane [torsion angles $C1-C2-C21-O22 = 169.25(16)^\circ$ and $C3-C4-N4-O42 = -174.03(18)^\circ$].

In the structure of the 1:1 INIPA salt with 4,5-dichlorophthalic acid, (II) (Fig. 2), one of the two primary piperidinium cation–anion associations also involves a secondary longer three-centre interaction [$N1A\cdots O12 = 3.042(4)$ Å and $N1A-H11A\cdots O12 = 117(3)^\circ$], which is probably an artefact of the overall cyclic hydrogen-bonding motif. This association [graph set $R_4^3(17)$] involves piperidinium–carboxylate $N-H\cdots O$, amide–carboxylate $N-H\cdots O$ and amide–amide $N-H\cdots O$ hydrogen bonds from two INIPA cations and one DCPA anion, and is closed by the intramolecular carboxy–carboxylate $O-H\cdots O$ hydrogen bond (Fig. 6). A second cyclic association [graph set $R_3^3(13)$] involves one piperidinium and two amide–carboxyl hydrogen bonds (Table 2), and the two motifs link the DCPA anions peripherally into head-to-head $N-H\cdots O$ amide-linked cation chain substructures. This results in one-dimensional ribbon structures which extend along the *b* cell direction. In the crystal structures of DCPA salts with Lewis bases, this low dimensionality in the hydrogen-bonded structures is commonly associated with the ‘planar’ DCPA monoanion, which features the cyclic intra-

Figure 7

A perspective view of the three-dimensional hydrogen-bonded framework structure of (III), showing the NIPA chain substructures and amide–amide dimer associations. Hydrogen bonds are shown as dashed lines. Graph sets for cyclic hydrogen-bonding associations are also indicated. Non-interactive H atoms have been omitted. [Symmetry code: (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; for other codes, see Table 3.]

short hydrogen bond [$2.393(3)$ Å] in the ‘planar’ DCPA anion in (II) results in a $C2-C1-C11-O11$ torsion angle of $174.1(3)^\circ$, while another feature of this conformation is elongation of the $C1-C11$ and $C2-C21$ bonds [$1.522(4)$ and $1.533(4)$ Å, respectively] and distortion of the external bond angles at $C1$ and $C2$ [$128.1(2)$ and $128.8(2)^\circ$, respectively; Smith & Wermuth, 2010*a*].

In the structure of the hydrogen 5-nitroisophthalate salt, (III) (Fig. 3), the primary cation–anion interaction has a second longer $N-H\cdots O_{\text{carboxylate}}$ contact [$N1A\cdots O12 = 3.0366(19)$ Å and $N1A-H12A\cdots O12 = 118.1(17)^\circ$], similar to that in (II). The cation–anion associations are also similar in some respects to those of (I). The hydrogen isophthalate anions give zigzag head-to-tail hydrogen-bonded chain substructures through carboxy–carboxylate $O-H\cdots O$ hydrogen bonds (Table 3) but these are classified as graph set $C(8)$, rather than $C(7)$ as in (I). In addition, the centrosymmetric $R_2^2(8)$ hydrogen-bonded INIPA amide–amide dimers give peripheral structure extension through piperidinium–carboxylate $N-H\cdots O$ hydrogen bonds which involve two anions, enclosing cyclic $R_3^3(10)$ rings (Fig. 7). The three-dimensional framework structure is generated through amide–carboxylate $N-H\cdots O$ hydrogen-bonding associations. The nitro O atoms are unassociated, except for weak intermolecular cation $C-H\cdots O$ associations [$C2A\cdots O52^{\text{ii}} = 3.308(2)$ Å and $C2A-H22A\cdots O52^{\text{ii}} = 151^\circ$] (see Table 3 for symmetry code). The anion in (III) is essentially planar, but with the carboxylate group rotated slightly out of the plane of the benzene ring [torsion angle $C2-C1-C11-O11 = -161.47(16)^\circ$, *cf.* $C2-C3-C31-O32 = 172.04(15)^\circ$ (the carboxylic acid group) and $C4-C5-N51-O52 = 175.06(17)^\circ$ (the nitro group)].

With the terephthalate salt, (IV), one of the piperidinium–carboxylate $N-H\cdots O$ hydrogen bonds seen in Fig. 4

Figure 8

The three-dimensional hydrogen-bonded framework structure of (IV), in a perspective view of the unit cell, showing hydrogen-bonding associations as dashed lines. Graph sets for cyclic hydrogen-bonding associations are also indicated. Non-interactive H atoms have been omitted. [For symmetry code (i), see Fig. 1; for other codes, see Table 4.]

is accompanied by an asymmetric three-centre piperidinium-carboxylate $N-H \cdots O/O'$ interaction [graph set $R_1^2(4)$] with the centrosymmetric terephthalate dianion (Fig. 8). This second association links two INIPA cations to the terephthalate dianion, which is extended longitudinally in the approximate b cell direction through centrosymmetric cyclic water-bridged amide-amide associations [graph set $R_4^4(12)$]. The water molecules also act as acceptors in bridging these chains laterally through amide $N-H \cdots O$ hydrogen bonds (Table 4), forming centrosymmetric cyclic $R_4^2(8)$ associations. The lateral piperidinium-carboxylate $N-H \cdots O$ hydrogen bonds shown in Fig. 4, together with the water-carboxylate $O-H \cdots O$ associations [graph sets $R_3^3(10)$, $R_3^3(18)$ and $R_6^4(22)$], complete a three-dimensional framework structure. The centrosymmetric terephthalate dianion deviates slightly from planarity [torsion angle $C2-C1-C11-O11 = 169.25(12)^\circ$].

The structures reported here further demonstrate the utility of the isonipecotamide cation as a synthon for the generation of stable hydrogen-bonded structures. An additional example of INIPA cation-anion association is also shown in the asymmetric three-centre piperidinium-carboxylate $N-H \cdots O/O'$ interaction in the first-reported structure of a 2:1 isonipecotamide carboxylate salt.

Experimental

The title compounds were synthesized by heating together under reflux for 10 min piperidine-4-carboxamide (isonipecotamide, 1 mmol) with either 4-nitrophthalic acid (1 mmol) for (I), 4,5-dichlorophthalic acid (1 mmol) for (II), 5-nitroisophthalic acid (1 mmol) for (III) or terephthalic acid (1 mmol) for (IV), in either methanol (50 ml) for (III), methanol-water (80%, 50 ml) for (I) and (IV), or ethanol-water (50%, 50 ml) for (II). After concentration to ca 30 ml, partial room-temperature evaporation of the hot-filtered solutions gave colourless plates of (I) and (III), blocks of (II) or prisms of (IV).

Table 1

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H11A \cdots O11^i$	0.98 (3)	1.77 (3)	2.729 (2)	163 (2)
$N1A-H12A \cdots O21$	0.93 (3)	1.92 (3)	2.803 (2)	158 (2)
$N41A-H42A \cdots O41A^{ii}$	0.92 (3)	1.99 (3)	2.907 (3)	176 (2)
$N41A-H43A \cdots O42^{iii}$	0.83 (3)	2.40 (3)	3.200 (3)	161 (3)
$O22-H22 \cdots O12^{iv}$	0.99	1.47	2.4562 (19)	179

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+2, -z+1$; (iii) $x-\frac{3}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

Compound (I)

Crystal data

$C_6H_{13}N_2O^+ \cdot C_8H_4NO_6^-$

$M_r = 339.31$

Monoclinic, $P2_1/n$

$a = 5.8637(5) \text{ \AA}$

$b = 11.2707(8) \text{ \AA}$

$c = 23.0268(19) \text{ \AA}$

$\beta = 93.082(8)^\circ$

$V = 1519.6(2) \text{ \AA}^3$

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.12 \text{ mm}^{-1}$

$T = 200 \text{ K}$

$0.40 \times 0.40 \times 0.12 \text{ mm}$

Data collection

Oxford Gemini-S CCD area-

detector diffractometer

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford

Diffraction, 2009)

$T_{\min} = 0.915$, $T_{\max} = 0.980$

10364 measured reflections

2989 independent reflections

2375 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.114$

$S = 1.05$

2989 reflections

233 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

$C_6H_{13}N_2O^+ \cdot C_8H_3Cl_2O_4^-$

$M_r = 363.19$

Monoclinic, $P2_1/n$

$a = 6.6897(4) \text{ \AA}$

$b = 9.7392(5) \text{ \AA}$

$c = 24.1222(13) \text{ \AA}$

$\beta = 92.479(4)^\circ$

$V = 1570.15(15) \text{ \AA}^3$

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.44 \text{ mm}^{-1}$

$T = 200 \text{ K}$

$0.30 \times 0.25 \times 0.20 \text{ mm}$

Data collection

Oxford Gemini S CCD area-

detector diffractometer

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford

Diffraction, 2009)

$T_{\min} = 0.908$, $T_{\max} = 0.980$

19231 measured reflections

3084 independent reflections

2777 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

Table 2

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H11A \cdots O11$	0.92 (4)	1.90 (4)	2.810 (3)	170 (3)
$N1A-H12A \cdots O22^i$	0.87 (4)	1.96 (4)	2.753 (3)	152 (3)
$N41A-H41A \cdots O21^{ii}$	0.82 (4)	2.48 (4)	3.158 (3)	142 (4)
$N41A-H42A \cdots O41A^{iii}$	0.93 (4)	2.19 (4)	3.086 (4)	163 (3)
$O12-H12 \cdots O21$	1.00	1.40	2.393 (3)	180

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Table 3

Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1A—H11A...O31 ⁱ	0.93 (2)	2.06 (2)	2.9236 (18)	153.6 (17)
N1A—H12A...O11	0.98 (2)	1.87 (2)	2.8229 (16)	164 (2)
N1A—H12A...O12	0.98 (2)	2.45 (2)	3.0366 (19)	118.1 (17)
N41A—H41A...O11 ⁱⁱⁱ	0.822 (19)	2.298 (19)	3.0669 (19)	155.9 (17)
N41A—H42A...O41A ⁱⁱⁱ	0.940 (19)	1.996 (19)	2.9321 (18)	174.1 (16)
O32—H32...O12 ^{iv}	0.93 (2)	1.63 (2)	2.5336 (17)	164 (3)

Symmetry codes: (i) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.113$
 $S = 1.30$
 3084 reflections
 224 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$

Compound (III)**Crystal data**

$\text{C}_6\text{H}_{13}\text{N}_2\text{O}^+ \cdot \text{C}_8\text{H}_4\text{NO}_6^-$
 $M_r = 339.31$
 Monoclinic, $P2_1/c$
 $a = 9.4117 (4) \text{ \AA}$
 $b = 14.3552 (5) \text{ \AA}$
 $c = 11.4490 (5) \text{ \AA}$
 $\beta = 103.787 (4)^\circ$
 $V = 1502.27 (11) \text{ \AA}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 200 \text{ K}$
 $0.45 \times 0.40 \times 0.18 \text{ mm}$

Data collection

Oxford Gemini-S CCD area-detector diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.980, T_{\max} = 0.990$
 9866 measured reflections
 2940 independent reflections
 2284 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.106$
 $S = 1.01$
 2940 reflections
 237 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Compound (IV)**Crystal data**

$2\text{C}_6\text{H}_{13}\text{N}_2\text{O}_8^+ \cdot \text{C}_8\text{H}_4\text{O}_4^{2-} \cdot 2\text{H}_2\text{O}$
 $M_r = 458.51$
 Triclinic, $P\bar{1}$
 $a = 6.5099 (5) \text{ \AA}$
 $b = 7.7777 (6) \text{ \AA}$
 $c = 11.6865 (12) \text{ \AA}$
 $\alpha = 76.429 (8)^\circ$
 $\beta = 76.968 (7)^\circ$
 $\gamma = 80.885 (7)^\circ$
 $V = 556.89 (9) \text{ \AA}^3$
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.11 \text{ mm}^{-1}$
 $T = 200 \text{ K}$
 $0.50 \times 0.15 \times 0.08 \text{ mm}$

Data collection

Oxford Gemini-S CCD area-detector diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.965, T_{\max} = 0.990$
 6562 measured reflections
 2177 independent reflections
 1746 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Table 4

Hydrogen-bond geometry (Å, °) for (IV).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1A—H11A...O11	0.966 (17)	1.856 (18)	2.7937 (16)	162.9 (14)
N1A—H12A...O11 ⁱ	0.979 (17)	1.847 (17)	2.8030 (15)	164.7 (17)
N1A—H12A...O12 ⁱ	0.979 (17)	2.367 (19)	3.1200 (16)	133.3 (14)
N41A—H41A...O1W ⁱⁱ	0.927 (17)	2.045 (17)	2.9181 (16)	156.5 (17)
N41A—H42A...O1W	0.95 (2)	2.111 (19)	2.9870 (17)	153.2 (14)
O1W—H11W...O41A ⁱⁱⁱ	0.861 (18)	1.892 (18)	2.7410 (15)	168.7 (17)
O1W—H12W...O12 ^{iv}	0.932 (19)	1.833 (19)	2.7632 (15)	175.6 (19)

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $-x+1, -y, -z+1$; (iii) $x+1, y, z$; (iv) $-x+1, -y+1, -z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.093$
 $S = 1.05$
 2177 reflections
 169 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$

H atoms involved in hydrogen-bonding interactions were located by difference methods and, with the exception of the carboxylic acid H atoms in (I) and (II), which were set to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ in the final cycles of refinement, their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinements at calculated positions (aliphatic C—H = 0.97 or 0.98 Å, and aromatic C—H = 0.93 Å) using a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For all four compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) for (I), (II) and (III); *SHELXS97* (Sheldrick, 2008) for (IV). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3064). Services for accessing these data are described at the back of the journal.

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